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(54) Title: GAS SENSOR

(57) Abstract

There is disclosed a gas sensor comprising an insulated gate FET in which the gate comprises one or more layers of a non–metallic gas sensitive material, the capacitance and/or the work function of said material being altered by exposure of said material to certain gases, and in which at least one layer of material is in direct contact with a gate insulating layer.

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GAS SENSOR

This invention relates to the field of gas sensing, in particular to a gas sensor comprising an insulated gate field effect transistor (FET) in which the gate comprises a gas sensitive material, with particular, but by no means exclusive, reference to semiconducting polymers.

The use of semiconducting polymers in gas detection is well established. Traditionally, transduction is achieved by exposing a semiconducting polymer, such as poly pyrrole, to the gas and measuring the accompanying changes in an impedance property of the polymer. The most widely used technique is one in which variations in the dc resistance of the polymer are measured (see, for example K C Persaud and P Pelosi in "Sensors and Sensory Systems for an Electronic Nose", pp 237-256, eds J W Gardner and P N Bartlett 1992, Kluwer Academic Publishers, Netherlands).

British Patent GB 2 203 553 describes an alternative technique in which changes in ac impedance are measured.

Devices based upon chemically induced changes in electron work function, so-called CHEMFETS, have been established for about 20 years. However, there appears to have been minimal interest in the possibility of fabricating semiconducting polymer CHEMFETS; in fact, there appears to be only one report of such an application - that of Joscowicz and Janata (M Joscowicz and J Janata, Anal. Chem. 58 (1986) 514). In this work, a rather complicated suspended gate gas sensitive Field Effect Transistor (gas FET) was described. Polymer (polypyrrole) was polymerised by connecting a suspended platinum gate mesh as the working electrode and electropolymerising around this mesh. The principle is essentially an adaption of the well-known technique of electropolymerisation across microgaps [5 to 20 μm] : the platinum mesh provides a plurality of such microgaps.

The present invention provides a semiconducting polymer insulated gate FET of straightforward design. The device offers numerous advantages over conventional semiconducting polymer gas sensor based upon the measurement of resistance changes. Furthermore, the device is of simple and more practical design compared to the device of Joscowicz and Janata, and is readily capable of supporting large (20 x 200 μm or greater) polymer coated gate dimensions. The present invention also provides gas sensors comprising insulated gate FETs having other gas sensitive materials.

According to a first aspect of the invention there is provided a gas sensor comprising an insulated gate FET in which the gate comprises one or more layers of a non-metallic gas sensitive material, the capacitance and/or the work function of said material being altered by exposure of said material to certain gases, and in which at least one layer of material is in direct contact with a gate insulating layer. Joscowicz and Janata provides details of the likely mechanism by which the changes in capacitance and/or work function enable gas detection to be accomplished.

The gas sensitive material may comprise semiconducting polymer. However, it is possible to utilise a variety of other materials such as liquid crystals, metal oxides, other polymers, semi-permeable materials, silicones and ceramics.

A first layer of semiconducting polymer in direct contact with the gate insulating layer may be deposited by chemical polymerisation. The chemical polymerisation may comprise : spin coating a gateless FET with a solution containing an oxidising agent; exposing the coated FET to monomer vapour; and etching the layer of polymer thus formed in an appropriate manner.

Alternatively, a first layer of semiconducting polymer in direct contact with the gate insulating layer may be deposited by photopolymerisation. The

photopolymerisation may comprise : spin coating a gateless FET with a photosensitive solution containing the monomers; exposing the coated FET to radiation of suitable wavelength to effect polymerisation and etching the layer of polymer thus formed in an appropriate manner.

The etching may comprise chemical etching.

The etching may comprise plasma etching.

The first layer of semiconducting polymer in direct contact with the gate insulating layer may be polypyrrole.

A second layer of semiconducting polymer may be deposited by electropolymerisation. The first layer of semiconducting polymer in direct contact with the gate insulating layer may be etched so as to create apertures in said first layer, said apertures permitting the second layer to be deposited in direct contact with the gate insulating layer.

The gas sensor may be an integral part of a CMOS, PMOS or NMOS device. The device may originally comprise at least one self-aligned polysilicon gate structure in which the polysilicon is removed and semiconducting polymer deposited in its place.

Active circuitry may be incorporated into the CMOS, PMOS or NMOS device.

Two insulated gate FETs may comprise a gas sensing arrangement in which the outputs of the first and second FET are differentially amplified, only the gas

sensitive material or materials of the first FET being exposed to the gas. The gas sensitive material or materials of the second FET may be encapsulated.

According to a second aspect of the invention there is provided a method for fabricating a gas sensor comprising the steps of : providing a gateless FET; and depositing one or more layers of a non-metallic gas sensitive material to form a gate, a first layer of said material being deposited so as to be in direct contact with a gate insulating layer; in which the capacitance and/or the work function of the gas sensitive material is alterable by exposure of said material to certain gases.

The gas sensitive material may comprise semiconducting polymer.

The first layer of semiconducting polymer in direct contact with the gate insulating layer may be deposited by chemical polymerisation or photopolymerisation.

The method may comprise the steps of :

spin coating a gateless FET with a solution containing an oxidising agent;

exposing the coated FET to monomer vapour; and

etching the layer of polymer thus formed in an appropriate manner.

The oxidising agent may be ferric chloride.

The method may comprise the steps of :

spin coating a gateless FET with a photosensitive solution containing the monomer;

exposing the coated FET to radiation of suitable wavelength to effect polymerisation; and

etching the layer of polymer this formed in an appropriate manner.

The etching may comprise chemical etching.

The etching may comprise plasma etching.

The first layer of semiconducting polymer may be polypyrrole.

The method may further comprise the step of depositing a second layer of semiconducting polymer by electropolymerisation. An electrical contact may be deposited onto the first layer of polymer, the electrical contact being used as a working electrode during electropolymerisation.

The first layer of semiconducting polymer may be etched so as to create apertures in said first layer, said apertures permitting the second layer of semiconducting polymer to be deposited in direct contact with the gate insulating layer.

Insulated gate FETs and methods for fabricating same in accordance with the invention will now be described with reference to the accompanying diagrams, in which:-

Figure 1 shows (a) a cross sectional side view and (b) a plan view of an insulated gate FET of the present invention; and

Figure 2 shows I vs V FET response characteristics with and without the presence of gas.

Figure 1 depicts a cross sectional view through a gas sensor of the present invention comprising an insulated gate FET 10 in which the gate 12 comprises a layer of semiconducting polymer 12a in direct contact with a gate insulating layer 14.

Figure 1 depicts a pMOS FET having a p+ source region 16 and a p+ drain region 18 formed in a n^- substrate 20. Electrical contacts 22, 24, 26 are made to the source, drain and gate regions respectively. The gate insulating layer 14 is a thin layer of SiO_2 although other insulating materials, such as silicon nitride, may be employed. It is understood that the invention is equally applicable to the manufacture of nMOS FETs.

The layer of semiconducting polymer 12a is deposited by chemical polymerisation. It is this step that enables the semiconducting polymer to be deposited in **direct contact** with the gate insulating layer 14, in contrast to the method of Joscowicz and Janata in which a complicated suspended gate configuration was adopted.

The chemical polymerisation comprises:
spin coating a gateless FET with a solution containing an oxidising agent;
exposing the coated FET to monomer vapour; and

etching the layer of polymer thus formed in an appropriate manner. This last step ensures that polymer remains deposited only in the gate area, over the gate insulating layer 14. Preferably, the gate area is protected by photolithographic techniques and 'surplus' polymer is removed by plasma or chemical etching. Polypyrrole is particularly suitable to act as the layer 12a, and ferric chloride is a particularly useful oxidising agent. Other oxidising agents, such as copper chloride, copper nitrate, would suggest themselves to skilled practitioners in the art.

Other methods of depositing a layer of semiconducting polymer in direct contact with the gate insulating layer 14 are within the scope of the invention. For example, the oxidising agent might be evaporated onto the surface of the FET, or spray or dip coating might be employed.

Alternatively, semiconducting polymer can be deposited by photopolymerisation. The photopolymerisation can comprise : spin coating a gateless FET with a photosensitive solution containing the monomer; exposing the coated FET to radiation of suitable wavelength (probably of UV wavelengths) to effect polymerisation; and etching the layer of polymer thus formed in an appropriate manner.

It is an important aspect of the invention that the above described deposition techniques are compatible with planar processing.

After deposition, an electrical contact is deposited onto the gate 12.

Advantageously, a second layer of semiconducting polymer is deposited by electropolymerisation. By producing a plurality of insulated FET devices of the present invention, in which each FET has a different second layer of polymer, the way is open to producing an array of gas sensors having different gas sensing sensitivities towards a wide range of gas and vapours. The second layer of polymer would be deposited onto a first layer such as polypyrrole, which acts as a excellent substrate and which adheres well to the gate insulating layer.

An electrical contact is deposited onto the first layer of semiconducting polymer, the electrical contact being used as a working electrode during electropolymerisation. A further advantage with this method is that deposition of, for example, a metal onto deposited polymer ensures that ohmic contact is made. A disadvantage is that the electropolymerisation process may attack the metal contact, which may necessitate the use of an appropriate mask prior to deposition of the second layer of polymer. Such is the case with aluminium. Methods for electropolymerising semiconducting polymers are well established in the literature : see, for example, International Publication WO 86/01599 and references therein.

Advantageously, the etching step described above is used to create apertures in the first layer of semiconducting polymer, the apertures permitting the second layer of semiconducting polymer to be electrochemically deposited in **direct contact** with the gate insulating layer. The advantage with this approach is that it avoids any possibility of cancellation of electron work function changes of the second layer of semiconducting polymer.

Insulated gate FETs of the present invention may be integrated into standard CMOS technology. It is well known that CMOS devices consume low amounts of power: possible applications of CMOS insulated gate FETs include low power badge mounted gas monitoring devices. Another advantage is that "active" circuitry may be incorporated into a CMOS device. Such active circuitry might control the application of voltages to the insulated gate FET or FETs and perform data pre-processing/processing. The active circuitry might also control the electropolymerisation of the second layer of polymer.

Insulated gate FETs of the present invention may be produced by "retrofitting" standard CMOS devices by removing self-aligned polysilicon gate structures and then depositing polymer in the manner described above. Gate dimensions are relatively large, typically 20 x 200 μm (length x width) but polypyrrole can be successfully deposited over such a surface. The gate would be well separated from other active circuitry : the gate interconnect would have to be routed over the chip final overlglaze to rejoin the on-chip circuitry.

The present invention also provides a gas sensing arrangement employing two insulated gate FETs, preferably of the same semiconducting polymer or polymers in which only the polymer(s) of one FET are exposed to the gas of interest. The outputs of the two FETs are differentially amplified. This arrangement minimises the effect of any FET response not caused by the presence of the gas, e.g. changes in FET

characteristics due to temperature drifts. Advantageously, the polymer or polymer of the FET not exposed to the gas is encapsulated with a suitable medium, such as an epoxy resin or a photoresist.

Insulated gate FETs of the present invention exhibit a number of advantageous features. Arrays of FETs may be produced which can be addressed by a suitable multiplexing arrangement and which exhibit differing sensitivities towards gases. The devices are inherently of relatively small dimensions. The FET devices are capable of flexible operation : current or voltage mode may be employed, using ac or dc waveforms. Since the device is a transistor, the effects of the work function variations are amplified by the device.

In Joscowicz and Janata a device is described which employs semiconducting polymer at the gate of a FET. However, the polymer is not in **direct contact** with the gate insulating layer : a rather complicated "suspended gate" arrangement is used. The device reported in Joscowicz and Janata is unquestionably of academic interest, however the configuration is impractical, as witnessed by the lack of any follow-up in the ten years since the publication of this paper. The present invention provides a practical configuration which can be made compatible with standard CMOS technology. As a result, devices of low cost and low power consumption may be produced. Furthermore, active circuitry can be incorporated into such devices.

It is possible to utilise other non-metallic gas sensitive materials which exhibit a change in capacitance and/or work function in the presence of gases. Such materials include liquid crystals, metal oxides, other polymers such as non-conducting polymers, semi-permeable materials, silicones and ceramics. The preferred methods of deposition depend upon the identity of the material selected.

Example

A device according the present invention was fabricated by modifying the gate structure of a PH sensitive ISFET. Polypyrrole is deposited in the following stages:

(i) the ISFET is cleaned with a suitable de-greasing solvent, rinsed in de-ionised water then methanol, and spun for 30 seconds at 2000 rpm to remove any surplus moisture;

(ii) a 4M solution of ferric chloride in iso-2-propanol is vacuum filtered and then spun onto the ISFET for 30 seconds at 2000 rpm.

(iii) 10-20 mls of pyrrole and 5-10 mls of de-ionised water are added to a petri-dish lined with filter paper (the water aids the reaction between the pyrrole vapour and the ferric chloride). The petri-dish is then transferred to a reaction chamber and left to stand for 10 minutes at room temperature.

(iv) the ISFET, now coated with ferric chloride, is transferred to the reaction chamber and left to stand for 15-30 minutes. Polymerisation with the ferric chloride results in a black film of polypyrrole over the entire substrate.

The polypyrrole is then etched in the following manner:

(v) a positive resist is spun at 2000 rpm for 30 seconds on top of the polypyrrole film and then baked.

(vi) aluminium is then evaporated onto the substrate and patterned using standard lithographic techniques to leave aluminium only in the gate region;

(vii) a plasma etch is performed in an oxygen plasma at a frequency of 400 kHZ and a power of 250W.

The use of aluminium is required because the etch rates of both polypyrrole and the positive resist have been found to be very similar. The use of a layer of resist between the aluminium mask and the polypyrrole is useful since it:

(i) protects the polypyrrole layer from contamination by the aluminium layer; and

(ii) allows the aluminium layer to be lifted off in acetone once the substrate has been plasma etched.

The device thus fabricated was exposed to n-butyl acetate vapour using a PTFE manifold that permits purging of the device with nitrogen gas. Figure 2 shows the effect of exposure to the vapour on the Ids-Vds characteristics of the device. Substantial changes - ca. 20% - are observed in drain current. The response to the vapour is fast. Furthermore, on purging with nitrogen the response returns or substantially returns to that originally observed in the absence of n-butyl acetate vapour.

CLAIMS

1. A gas sensor comprising an insulated gate FET in which the gate comprises one or more layers of a non-metallic gas sensitive material, the capacitance and/or the work function of said material being altered by exposure of said material to certain gases, and in which at least one layer of material is in direct contact with a gate insulating layer.

2. A gas sensor according to claim 1 in which the gas sensitive material comprises semiconducting polymer.

3. A gas sensor according to claim 2 in which a first layer of semiconducting polymer in direct contact with the gate insulating layer is deposited by chemical polymerisation.

4. A gas sensor according to claim 3 in which the chemical polymerisation comprises: spin coating a gateless FET with a solution containing an oxidising agent; exposing the coated FET to monomer vapour; and etching the layer of polymer thus formed in an appropriate manner.

5. A gas sensor according to claim 2 in which a first layer of semiconducting polymer in direct contact with the gate insulating layer is deposited by photopolymerisation.

6. A gas sensor according to claim 5 in which the photopolymerisation comprises: spin coating of gateless FET with a photosensitive solution containing the monomer; exposing the coated FET to radiation of suitable wavelength to effect polymerisation; and etching the layer of polymer thus formed in an appropriate manner.

7. A gas sensor according to claim 4 or claim 6 in which the etching comprises chemical etching.

8. A gas sensor according to claim 4 or claim 6 in which the etching comprises plasma etching.

9. A gas sensor according to any of the previous claims in which the first layer of semiconducting polymer in direct contact with the gate insulating layer is polypyrrole.

10. A gas sensor according to any of the previous claims having a second layer of semiconducting polymer is deposited by electropolymerisation.

11. A gas sensor according to claim 9 in which a first layer of semiconducting polymer in direct contact with the gate insulating layer is etched so as to create apertures in said first layer, said apertures permitting the second layer of semiconducting polymer to be deposited in direct contact with the gate insulating layer.

12. A gas sensor according to any previous claims as an integral part of CMOS, PMOS or NMOS device.

13. A device according to claim 12 originally comprising at least one self-aligned polysilicon gate structure, in which the polysilicon is removed and semiconducting polymer deposited in its place.

14. A device according to claim 12 or claim 13 in which active circuitry is incorporated therein.

15. A gas sensing arrangement in which the outputs of a first and second insulated gate FET according to any of the previous claims are differentially amplified, only the gas sensitive material or materials of the first FET being exposed to the gas.

16. A gas sensing arrangement according to claim 15 in which the gas sensitive material or materials of the second FET are encapsulated.

17. A method for fabricating a gas sensor comprising the steps of:

providing a gateless FET; and depositing one or more layers of a non-metallic gas sensitive material to form a gate, a first layer of said material being deposited so as to be in direct contact with a gate insulating layer; in which the capacitance and/or the work function of the gas sensitve material is alterable by exposure of said material to certain gases.

18. A method according to claim 17 in which the gas sensitive material comprises semiconducting polymer.

19. A method according to claim 18 in which the first layer of semiconducting polymer in direct contact with the gate insulating layer is deposited by chemical polymerisation or photopolymerisation.

20. A method according to claim 19 comprising the steps of:

spin coating a gateless FET with a solution containing an oxidising agent; exposing the coated FET to monomer vapour; and etching the layer of polymer thus formed in an appropriate manner.

21. A method according to claim 20 in which the oxidising agent is ferric chloride.

22. A method according to claim 19 comprising the steps of:

spin coating a gateless FET with a photosensitive solution containing the monomer;

exposing the coated FET to radiation of suitable wavelength to affect polymerisation; and

etching the layer of polymer thus formed in an appropriate manner.

23. A method according to any of claims 20 to 22 in which the etching comprises chemical etching.

24. A method according to any of claims 20 to 22 in which the etching comprises plasma etching.

25. A method according to any of claims 19 to 24 in which the first layer of semiconducting polymer is polypyrrole.

26. A method according to any of claims 19 to 25 further comprising the step of depositing a second layer of semiconducting polymer by electropolymerisation.

27. A method according to claim 26 in which an electrical contact is deposited onto the first layer of polymer, the electrical contact being used as a working electrode during electropolymerisation.

28. A method according to claim 26 or claim 27 in which the first layer of semiconducting polymer is etched so as to create apertures in said first layer, said apertures permitting the second layer of semiconducting polymer to be deposited in direct contact with the gate insulating layer.

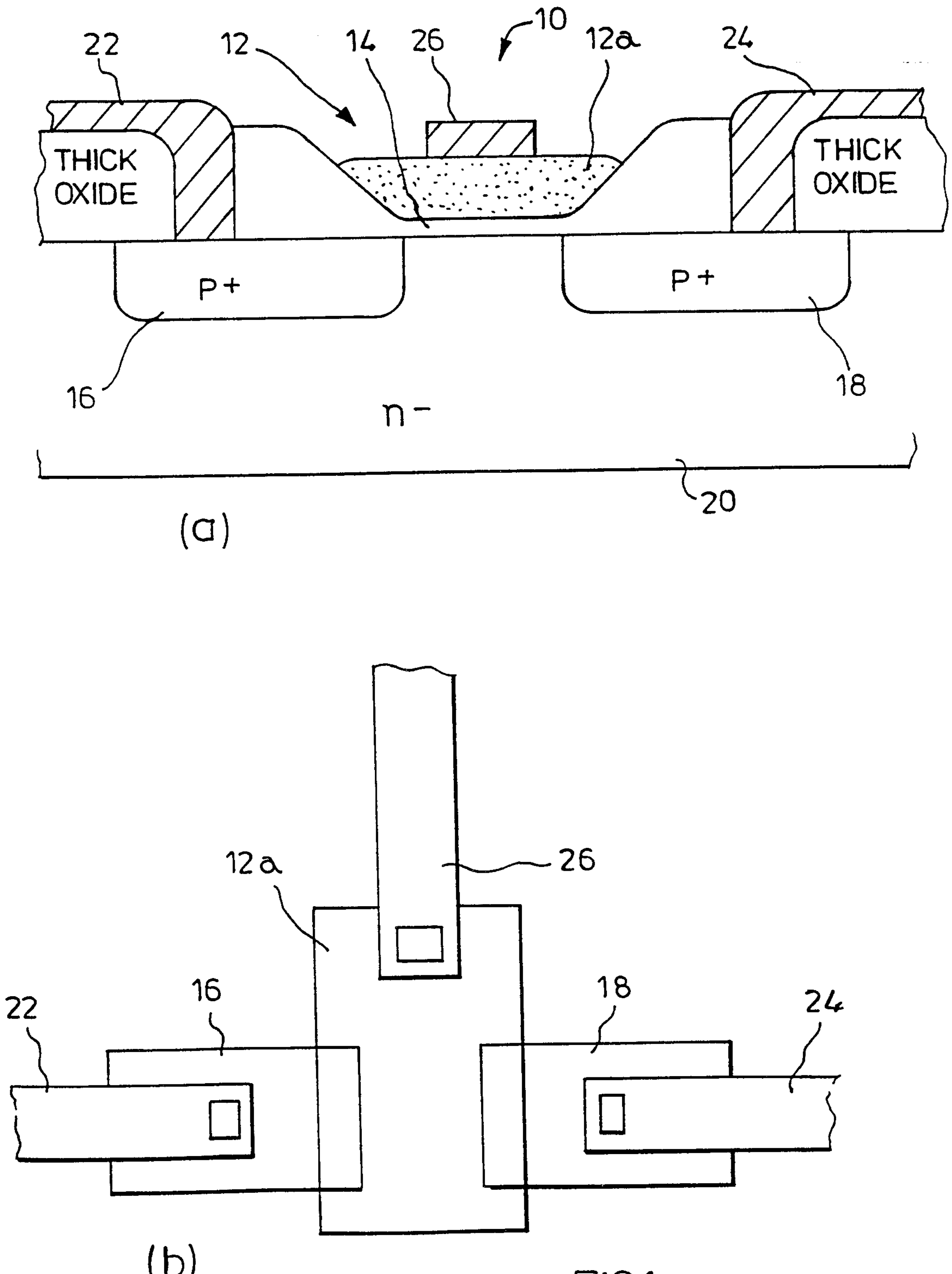
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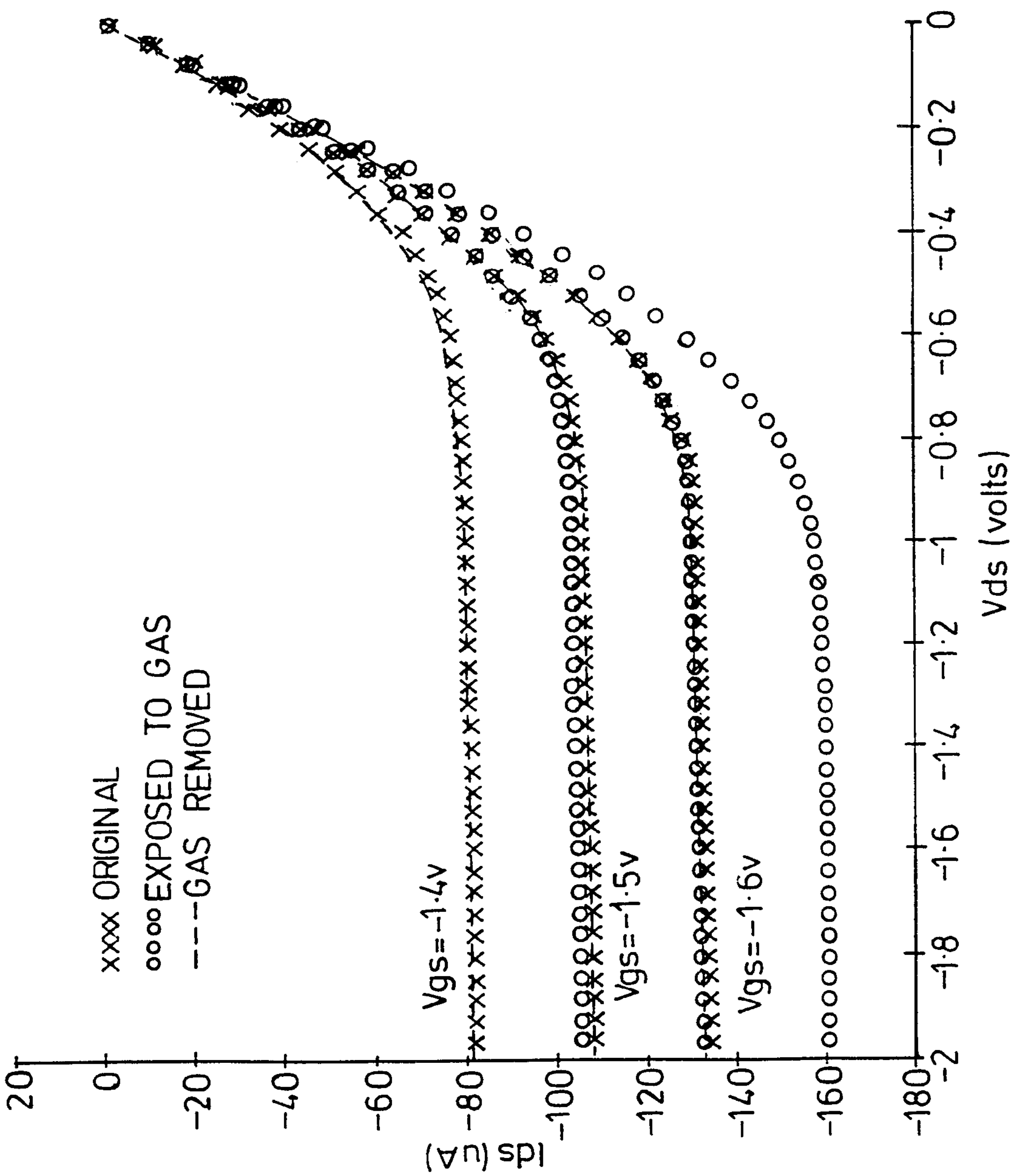
FIG.1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Vgs=-1.5v
Vgs=-1.6v
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FIG.2

INTERNATIONAL SEARCH REPORT

In ational Application No
PCT/GB 98/00776

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N27/414

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	WO 87 00633 A (FRAUNHOFER GES FORSCHUNG) 29 January 1987 see page 10, line 1 - line 28; figure 6 ---	1,17
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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24 June 1998	03/07/1998

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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